

New Phases of Solid Nitrogen

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We report the discovery of a new class of molecular phases of solid nitrogen at high pressures and temperatures by Raman and infrared spectroscopy and powder x-ray diffraction. Unlike the molecular phases consisting of disk- and sphere-like molecular disorder (δ -, ϵ - and ζ -N₂) and reportedly stable over a wide P-T range, one of the new phases (ι) is diatomic with disk-like molecules. A second new phase (the higher pressure θ -phase) is characterized by strong intermolecular interactions and infrared vibron absorption. Both phases exhibit wide P-T ranges of stability and metastability.

The evolution of molecular solids under pressure constitutes an important problem of modern physics [1]. Under compression, delocalization of electronic shells and eventual molecular dissociation with formation of a framework or closed packed structures is expected. This pathway is not necessarily a straightforward process, because of large barriers of transformation between states with different types of bonding and molecular structures with various types of orientational order, including possible dimers or associated and charge transfer compounds. Nitrogen is an archetypal homopolar diatomic molecule with a very strong intramolecular bonding. The phase diagram of nitrogen is complex at moderate pressures and temperatures and has been little studied over a wider range until recently [2]. A theoretically proposed dissociation of nitrogen molecules under pressure [3] recently was confirmed experimentally [4,5]. Our previous study [6] suggests that the nonmolecular material obtained on cold compression is amorphous, formed as a consequence of the large barrier of transformation to the crystalline phase. Here, we report the existence of two new molecular phases, called ι and θ , which have exceptionally large region of stability and metastability extending through the P-T region where ϵ and ζ have been thought to be the only stable phases of nitrogen. This observation establishes a new class of dense solid molecular N₂ phases.

The phase diagram of nitrogen is shown in Fig. 1. The melting curve was measured up to 900 K [7]; from liquid phase, which exists to 2 GPa at room temperature, nitrogen solidifies in a disordered (plastic) β phase, which is a common feature of diatomic molecular crystals [8]. Low pressure and temperature α and γ phases represent two ways of packing quadrupoles [8]. At higher pressures, another class of structures with non quadrupolar-type ordering was discovered (δ , δ_{loc} , ϵ , ζ) [9–13]. This happens because the relative contribution of the quadrupolar interactions gradually decrease, and other interactions (e.g., short-range repulsive) come to play. The δ phase is disordered with sphere- and disk-like types of molecules orientationally distributed between corners and faces of a fcc unit cell (space group Pm3n) [12]. With decreasing

temperature and/or increasing pressure molecules partially order in δ_{loc} -N₂ phase and then completely in ϵ -N₂. The latter has a distorted cubic (rhombohedral space group R3c) structure as determined from in situ x-ray measurements [13]. Vibrational spectroscopy shows that this phase preserves the difference between sphere- and disk-like molecules. Further increase in pressure leads to several sequential changes in vibrational spectra, namely increase of a number of the lattice modes and branching of vibron mode corresponding to disk-like molecules [14,15]. With a lack of decisive x-ray data [16], these transformations have been interpreted as due to a further lowering of symmetry [10]. The available data indicate that only ζ phase can be considered as well established molecular phase at higher pressures [15]. The transformation to this phase is quite pronounced at 21–25 GPa at low temperatures [10], but at room temperature the changes in vibrational spectra are relatively subtle [14,15]. Theoretical calculations confirm the stability of ϵ phase as the ordered phase from 2 to 41.5 GPa [17], although simulations [18] favor tetragonal multimolecular structures, which disagree with the known experimental data at the same pressure range.

The P-T region, of the phases derived from δ -N₂ (δ_{loc} , ϵ , ζ) are observed is quite wide (Fig. 1), apparently extending to the transition to nonmolecular phase η [4,6]. For comparison, γ -O₂, a structural analog of δ -N₂ (see also β -F₂ and CO [12]) is stable in a relatively narrow PT range, beyond which structures with collinear molecules become energetically favorable (O₂,F₂) [12] or chemical dissociation takes place CO). Although the above molecular crystals are different from the point of view of anisotropic intermolecular forces [12], one would expect that at high density the most effective packing of dumbbell molecules remains the dominant term in determining phase stability prior to dissociation.

Prior to the transition to nondiatomic phase, the Raman vibron shows a substantial softening [14–16] which can arise from weakening of the intramolecular bond but can also arise from increased vibrational splitting. Information about the vibron frequencies and their pressure

dependence in different ordered molecular phases is important for understanding of the nature of this ordering. For example, an abrupt drop in the vibrational frequency at a structural transition can be due to delocalization of the intramolecular bonding charge giving possible dimer formation [19] and/or charge transfer phases [20]. At the transition to the nonmolecular phase, the lattice excitations and vibrons are replaced by new excitations, consistent with nondiatomic structure [4,6]. Detailed study of vibrational properties and structure of semiconducting absorption edge suggests disorder, at least for certain P-T paths followed to create the material [6]. In order to establish the relation between molecular and non-molecular phases we examined nitrogen from 15 to 1000 K and up to 150 GPa using different experimental techniques including *in situ* high-temperature visible and Raman spectroscopy as well IR [21]synchrotron spectroscopy and x-ray synchrotron diffraction used on samples quenched to the room temperature (RT).

When compressed at RT nitrogen transforms from the ϵ to ζ phase around 60 GPa (see Fig. 1) [22]. When heated, sample first back transforms from ζ to ϵ phase along the boundary, which we find to be on the extension of the line established in Ref. [2] at lower temperatures. When temperature reaches \sim 625 K phase transition to θ nitrogen takes place. The transition can be observed visually (see inset to Fig. 1) since ϵ -N₂ normally shows a substantial grain boundaries, while after transition to the θ phase, the sample looks uniform and translucent. In most cases the transition happens instantaneously and completely (determined by Raman spectroscopy) within seconds. If ϵ -N₂ is heated at even lower pressures (e.g., 60-70 GPa), it transforms above 750 K to ι -N₂. It is also possible to access ι phase from θ . In one of our experiments we observed the transformation from the θ to ι phase on pressure release at \sim 850 K at 69 GPa.

Fig. 2 shows the Raman and IR absorption spectra of the θ and ι phases quenched to room temperature. The spectrum of the ζ phase (initial material) obtained by "cold" compression is shown for comparison. The Raman and IR spectra of both the θ and ι phases exhibit vibron modes, although their number and frequencies differ from those of all other known molecular structures (see below). The infrared vibron mode of the θ phase has much larger oscillator strength compared to other N₂ phases (cf. H₂ in phase III [23] and ϵ -O₂ [19]). The lattice modes of θ nitrogen are very sharp compared to either ι or ζ (ϵ). This is a clear indication that molecular ordering in θ phase is essentially complete, whereas other molecular phases still possess substantial amount of static or dynamic orientational disorder. Comparison of Raman and infrared vibron modes shows a general softening of the vibron bands of θ nitrogen compared to the other modifications (ι, ζ, ϵ). This fact and also a presence of relatively strong infrared vibron band indicate a charge transfer from intra- to intermolecular bonds and

strengthen our arguments about ordered nature of the phase [19,20]. Raman and infrared spectra show several cases of frequency coincidence of Raman and infrared vibron and lattice modes, which excludes an inversion center for both structures.

The pressure dependence of the Raman-active vibron modes (Fig. 3) was studied on unloading at 300 K in both phases (see discussion below). ι -N₂ exhibits a typical behavior for molecular crystals: branching of vibrational modes and increasing of separation between them with pressure due to increasing of intermolecular interactions. All the vibrational modes originate from the same center, which is close to the frequency of the ν_2 disk-like molecules in ϵ -N₂. Thus, the structure of the ι phase is characterized by presence of just one type of site symmetry occupied by the molecules, and a large number of vibrational modes arise from a large unit cell (a minimum 8 molecules per cell). For the θ phase, two different site symmetries appear to be occupied. The higher frequency $\nu_{1\theta}$ gives rise to three Raman bands and one IR, while the lower frequency of $\nu_{2\text{theta}}$ - correlates with only one Raman band.. Detailed analysis of vibratioanal spectra of both θ and ι phases will be published elsewhere.

Synchrotron x-ray diffraction data (Fig. 4) confirm the existence of two new structures. First, the data show a good agreement with previously reported results for the ϵ -phase [24,25]. Only a few reflections could be observed above 50 GPa because of a strong sample texture. No major changes in the x-ray diffraction patterns were observed at 60 GPa and room temperature, corresponding to the ϵ – ζ transition (see also Ref. [16]). This observation is consistent with vibrational spectroscopy, which shows only moderate changes identified as a further distortion of the cubic unit cell of the δ phase [14,22]. In contrast, the x-ray diffraction patterns of the samples after ζ – θ and ζ – ι transformations differ substantially from those of the ϵ and ζ phases, and from each other (Fig. 4). Indexing of the peaks of θ nitrogen shows that its unit cell is orthorhombic, for example with the lattice parameters $a=6.797(4)$, $b=7.756(5)$ and $c=3.761(1)$. The systematic absences, lack of inversion center and presence of high-symmetry sites (see above) are consistent with the space groups Pma2, Pmn21, Pmc21, Pnc2, P21212. The a/c ratio is close to $\sqrt{3}$, which clearly suggests that the lattice is derived from a hexagonal structure (cf. hydrogen in phase III). Extrapolation of the equation of state of ϵ -N₂ measured to 40 GPa [24] shows that the molecular volume for this phase is about $14 \text{ \AA}^3/\text{molecule}$ at 95 GPa, which gives an upper bound assuming a pressure-induced (density driven) transition. Comparison with the experimentally determined unit cell volume (198 \AA^3) suggests 16 molecules in the unit cell, giving 12.4 \AA^3 per molecule in the θ -phase and 11% volume collapse at the ϵ – θ transition. The number of molecules is in agreement with vibrational spectroscopy data, although it is possible to describe the vibrational spectra with smaller number (up

to 8).

In order to better understand the provenance of new phases in the phase diagram and their relation with other phases of nitrogen (Fig. 1), we pursued extensive observations in different parts of the phase diagram. The new phases have a wide range of stability or metastability. As it was noted above, both phases could be quenched to room temperature. On subsequent heating, the θ -phase remained stable when heated above 1000 K between 70-135 GPa, but it transforms to ι -N₂ when releasing pressure at 68 GPa at 850 K (see above). In view of the relatively high temperature of this transformation and its absence at room temperature, this observation implies that transformation point is close to the thermodynamical $\theta - \iota$ transition (see Fig. 1). At room temperature, θ nitrogen remains metastable as low as 30 GPa on unloading. Similarly, the ι -N₂ remains metastable to 23 GPa; at these pressures both phases transform to ϵ -N₂ on unloading. ι -N₂ was found to be stable at low temperatures (down to 10 K) at pressures as low as 30 GPa. It is interesting to note that amorphous η nitrogen can be accessed only from ζ -N₂ (see Fig. 1). The apparent kinetic boundary, that separates these phases can be treated as a line of instability of ζ -N₂. On the other side, the ι and θ phases can be reached from ϵ (and maybe δ) phase only. We observed that on further increasing of pressure and temperature θ phase does not transform to the nonmolecular phase η (to at least 135 GPa and 1050 K). We suggest that, it might instead transform to a (perhaps different) nonmolecular crystalline phase on compression. By this argument, this phase cannot be reached by "cold" compression because of the kinetic barrier separating it from ζ -N₂. Also, one can speculate that heating of the amorphous phase can help to overcome the energy barrier and induce its crystallization.

The data presented allow us to speculate about the nature of ι and θ nitrogen and their large metastability on unloading. The ι -phase consists of disk-like molecules, presumably packed more efficiently compared to the mixed disk- and sphere-like δ -family structures. The θ -phase is more complex; it is very tempting to interpret this phase as due to formation of polyatomic molecules (e.g. N₂-N₅), as has been suggested by theoretical calculations [26]. The striking vibrational properties of θ nitrogen strongly suggest some kind of associated phase, perhaps with some analogy to H₂-III [27], ϵ -O₂ [19] or CO₂-II [28]. The phase diagram of nitrogen appears to be very complex. The presence of substantial barriers of transformations makes the transformations very sluggish. Thus, determination of the thermodynamical boundaries between phases requires additional studies. The data obtained in this study clearly show that the new phases are thermodynamically stable high-pressure phases. This conclusion is based on the fact that the same phase is formed irrespective of the thermodynamic path. Moreover, the ζ -N₂ seems to be metastable, since

it can be obtained only as a result of "cold" compression of the ϵ -N₂ (see also Refs. [6,22]).

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FIG. 1. Phase diagram of nitrogen. Filled symbols and thick solid lines are the data from this work and Refs. 6,22. Dashed-dotted line is the proposed extension of the $\zeta - \eta$ transition boundary (see text). Open circles and short dashed line are from visual observations of Ref. 5. Phase boundaries at low pressures are from Refs. 2,7. The phase boundaries for α, γ, δ and δ_{loc} phases are not shown. The inset shows the photo of theta phase at 95 GPa and 300 K.

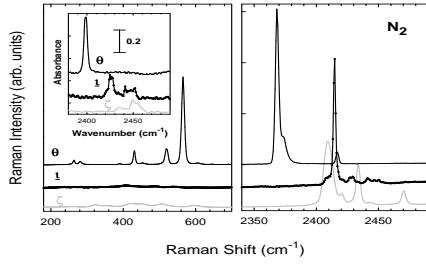


FIG. 2. Representative Raman and IR spectra (inset) of θ (solid lines) and ι (lines with dots) phases measured at 95 and 70 GPa and 297 K upon quenching from high temperature (see text). The spectra of ζ phase (gray lines) are shown for comparison.

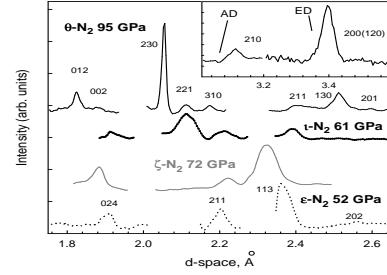


FIG. 4. X-ray diffraction patterns of θ (solid lines), ι (lines with dots), ζ phase (gray lines) and ϵ (dashed lines) measured at different pressures and 297 K. AD and ED stand for angle- and energy-dispersive techniques, respectively. The diffraction lines corresponding to rhenium were subtracted. The corresponding d-space ranges are omitted. Indexing of ϵ -N₂ pattern is according to Ref. 24.

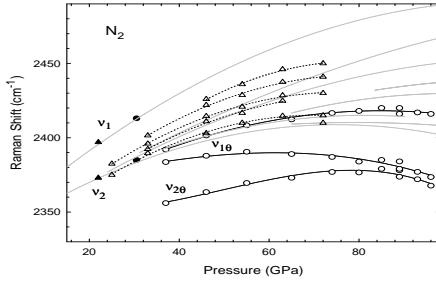


FIG. 3. Raman frequencies of vibron modes as a function of pressure for θ (open circles and solid lines) and ι (open triangles and dashed line) phases measured at the pressure release. Filled circles and triangles correspond to the vibron frequencies after transformation to the ϵ phase from θ and ι phases, respectively. Gray lines are data for $\epsilon(\zeta)$ phases from Ref. 15.